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Learn About ...

CARBON DIOXIDE

Atmospheric Carbon Dioxide

Carbon dioxide, CO_2, is one of the gases in our atmosphere. Both natural processes and human activities contribute to its presence at a present concentration of about 0.040% [406 parts per million (ppm) on January 7, 2017], uniformly distributed over the Earth. Commercially, CO_2 finds uses as a refrigerant (dry ice is solid CO_2), in beverage carbonation, and in fire extinguishers. Because the concentration of CO_2 in the atmosphere is low, no practical process has yet been developed to obtain the gas by extracting it from air. Most commercial CO_2 is recovered as a by-product of other processes, such as the production of ethanol by fermentation and the manufacture of ammonia. Some CO_2 is obtained from the combustion of coke or other carbon-containing fuels.

$$C(coke) \; + \; O_2(g) \rightarrow CO_2(g)$$
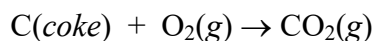
Carbon dioxide is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. As a result of the tremendous world-wide consumption of such fossil fuels, the amount of CO_2 in the atmosphere has increased over the past two centuries, now rising at a rate of about 2-3 ppm per year, Figure 1.
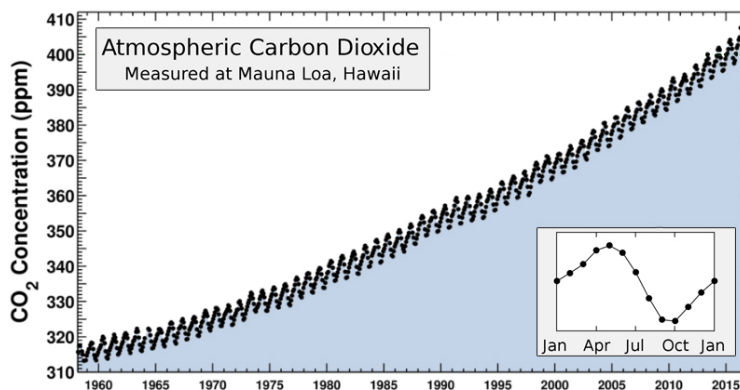

Figure 1. This is the Keeling curve, named for the scientist, Charles Keeling, who began systematic monitoring of the atmospheric CO_2 concentration at a site on the top of the Mauna Loa volcano in Hawaii in 1957. These are the usual measurements quoted in news reports and articles on atmospheric CO_2 levels. Other stations around the world are now also monitoring atmospheric CO_2, but Keeling's are the longest continuous measurements. The annual variation shown in the inset is discussed below.

Graph taken from scripps.ucsd.edu in February, 2017.

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Carbon Dioxide: Earth's Thermostat

The greenhouse effect is a vitally important phenomenon that keeps the Earth warm enough to evolve and sustain life, as we know it. Carbon dioxide is one of the most important greenhouse gases that cause warming of the planet. Without the atmospheric carbon dioxide, the Earth's average temperature would be about 255 K (–18 °C), an ice ball; there would be no liquid water. How can a gas that makes up less than one tenth of a percent of the atmosphere have such a profound effect?

The source of almost all the energy on Earth is the sunlight that falls on and warms its surface. In order to maintain a constant average temperature, the surface emits energy back into space. You can see the sunlight, but you can't see the radiation emitted by the Earth, because it is infrared light your eyes can't detect. You can, however, feel it. Hold your hand over a dark surface, like an asphalt parking lot, in the evening after a warm sunny day and your hand feels warm. Infrared light emitted by the surface warms your skin. The higher the temperature of the surface, the more infrared light it emits and the warmer it feels.

Just as the molecules in your skin absorb infrared light, almost all other molecules also absorb infrared light. The exceptions are diatomic molecules containing only one element (homonuclear diatomics), such as O_2 and N_2 (and atomic species like argon, Ar), the gases that make up almost 100% of dry air. If these were the only components of the atmosphere, the infrared light from the surface would all escape into space. But there have always been traces of other gases in the atmosphere, carbon dioxide, CO_2, methane, CH_4, and nitrous oxide, N_2O, for example. And, since water, H_2O, on the surface evaporates, there is water vapor (humidity) adding a great deal to the greenhouse effect. All of these gases absorb infrared light. So what is necessary for a molecule to absorb infrared light and why does it matter for the Earth's climate?

The energies of infrared wavelengths of light are in the energy range that can cause vibrations among the atoms and bonds that make up molecules. In order for the light to interact with the molecular vibration, the movement has to change the dipole moment of the molecule. Changes in the dipole moment for the vibrations of the CO_2 molecule are represented in Figure 2. The molecule does not have a permanent dipole moment, but its electrons are not equally shared between the carbon and oxygen atoms. When the molecule bends or when it undergoes an asymmetric stretch, its dipole moment changes from zero to a nonzero value and these vibrations absorb some wavelengths of infrared light. All molecules with three or more atoms (as well as heteronuclear diatomics, NO or CO, for example) absorb some wavelengths of infrared light.
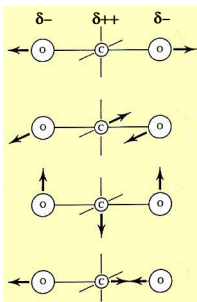
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Figure 2. The vibrations of the CO_2 molecule involve the atomic movements shown by the arrows in these diagrams. Charge separation in the molecule is exactly balanced along the linear molecule, so it has no permanent dipole moment. The symmetric stretch (top) does not change the balance; this vibration does not absorb infrared radiation. Bending out of the line (middle two) or asymmetric stretch (bottom) does change the charge balance; these vibrations absorb infrared.

Molecules that are good infrared absorbers also readily emit the extra energy as infrared light in all directions. Infrared light leaving the Earth's surface is all going essentially up and out toward space. If some of it is absorbed and re-emitted in all directions by atmospheric greenhouse gases, less of what leaves the surface will make it out into space. That means the planet would not be in energy balance, because there would be more energy coming in from sunlight than infrared energy leaving. To compensate, the surface could get warmer, so more infrared light would leave the surface and enough of this would reach space to balance the incoming sunlight. "Trapping" some energy from Earth's infrared emission, is the essence of the atmospheric greenhouse effect that has warmed Earth to average temperatures that support its abundance of life.

In the absence of modern industrial human activity, the surface and atmosphere maintained a steady state with a relatively constant amount of CO_2, about 280 ppm, for several millennia before the invention of the steam engine. Over hundreds of millennia, the atmospheric CO_2 concentration (and Earth's temperature) has varied naturally, Figure 3, mainly triggered by variations in the Earth's tilt and its orbit around the sun. The natural state of the climate for the past million years or more has been cold (glacial ice ages) with periodic warm (interglacial) periods. Human civilization developed during this latest warm period, which would naturally be heading (slowly) toward the next ice age, if humans were not adding CO_2 (and other greenhouse gases) to the atmosphere. Instead the average global temperature has increased by about 1 °C since the Industrial Revolution. (This might seem like a trivial change, but a *drop* in average temperature of 2 or 3 °C would put us in an ice age.) Changes in global climate have already resulted from our addition of CO_2 to the atmosphere, with its consequent global warming, and will increase in severity with a continued increase in CO_2 concentration.

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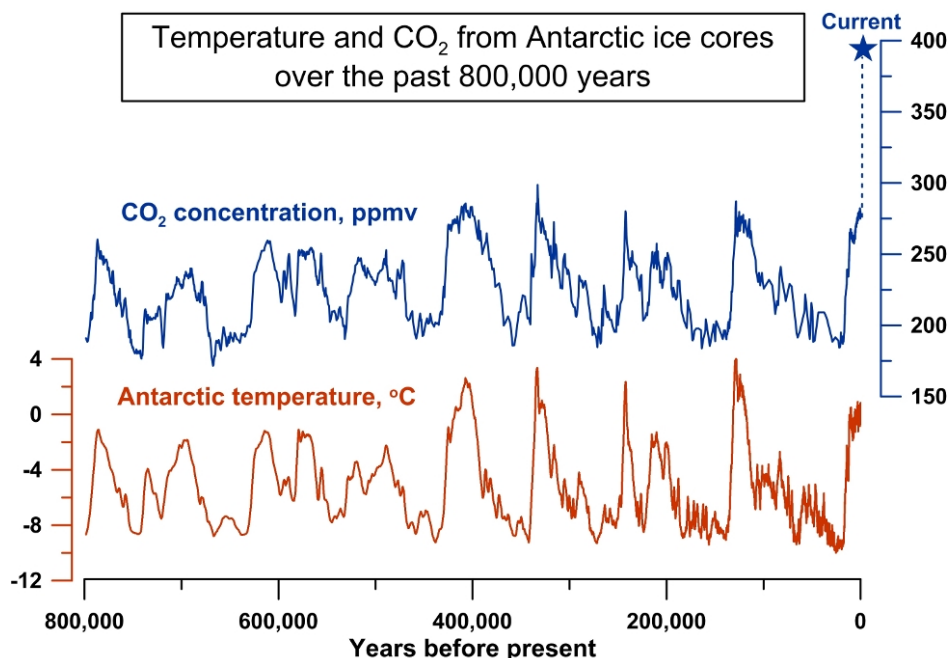in the Lab of Shakhashiri
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Figure 3. Data derived from the gases trapped in ice cores bored out of the kilometers thick ice sheets on Antarctica (and Greenland) tell us how Earth's temperature and atmospheric CO_2 varied over the past 800,000 years.

Graphic from simpleclimate.wordpress.com.
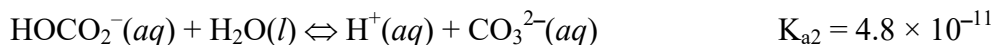
Aqueous Solutions of Carbon Dioxide

In addition to being a component of the atmosphere, CO_2 also dissolves in the water of the oceans. (About one-quarter of the CO_2 emitted by human activity ends up in the oceans; see more below.) At room temperature, the solubility of CO_2 is about 90 cm^3 of CO_2 (about 0.16 g) per 100 mL of water. In aqueous solution, CO_2 exists in many forms. First, it dissolves.

$$CO_2(g) \Leftrightarrow CO_2(aq)$$
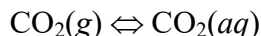
In fresh water, almost all the dissolved CO_2 is present as $CO_2(aq)$ in equilibrium with the $CO_2(g)$ in contact with the solution. Reaction with water establishes another equilibrium between the dissolved CO_2 and hydronium [H_3O^+ or $H^+(aq)$] and hydrogen carbonate (bicarbonate, HCO_3^- or $HOCO_2^-$) ions.

$$CO_2(aq) + H_2O(l) \Leftrightarrow H^+(aq) + HOCO_2^-(aq) \qquad K_{a1} = 4.2 \times 10^{-7}$$

The equilibrium constant is labeled K_{a1}, because it is the first step in the acid-base reaction of CO_2 with water. The second step produces hydronium and carbonate, CO_3^{2-}, ions.

$$HOCO_2^-(aq) + H_2O(l) \Leftrightarrow H^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 4.8 \times 10^{-11}$$

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You will sometimes see the chemistry of dissolved CO_2 characterized in terms of carbonic acid, H_2CO_3 or $(HO)_2CO$. But almost none of the dissolved CO_2 exists as $(HO)_2CO$, so the first acid-base equilibrium is best represented, as above, in terms of $CO_2(aq)$.

A solution of CO_2 dissolved in pure water is mildly acidic (relatively low concentration of hydronium ions), from the first acid-base equilibrium, and also contains about the same (low) concentration of hydrogen carbonate anions. Because the concentration of $HOCO_2^-(aq)$ anions is low and K_{a2} is small, the solution contains essentially no carbonate anions, $CO_3^{2-}(aq)$. The situation is quite different for CO_2 dissolved in seawater.
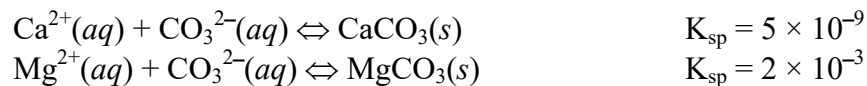
Seawater contains many ionic species, including those from dissolved CO_2, that make the solution slightly basic (more hydroxide ions, OH^-, than hydronium ions). As CO_2 dissolves in seawater, the hydronium ions formed by its reaction with water react with hydroxide and drive the reaction to form $HOCO_2^-(aq)$ and decrease the amount of $CO_2(aq)$. The overall process can be represented by this reaction, where the equilibrium lies far to the right.

$$CO_2(aq) + OH^-(aq) \Leftrightarrow HOCO_2^-(aq)$$
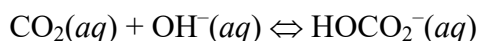
Similar chemistry leads to the reaction of $HOCO_2^-(aq)$ with $OH^-(aq)$ to form $CO_3^{2-}(aq)$.

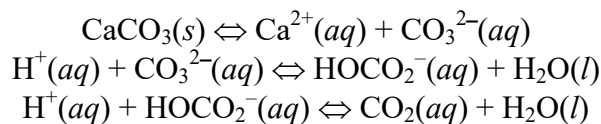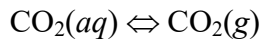$$HOCO_2^-(aq) + OH^-(aq) \Leftrightarrow H_2O(l) + CO_3^{2-}(aq)$$
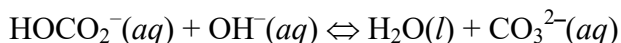
The upshot of these equilibrium reactions is that the CO_2 in seawater exists as a tiny amount of $CO_2(aq)$ [in equilibrium with atmospheric $CO_2(g)$], about 90% $HOCO_2^-(aq)$ and 10% $CO_3^{2-}(aq)$. The carbonate anions interact with cations in seawater. According to the solubility rules, "all carbonates are insoluble except those of ammonium and Group IA elements." Therefore, the carbonate ions cause the precipitation of certain ions. For example, Ca^{2+} and Mg^{2+} ions precipitate from seawater as carbonates.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \Leftrightarrow CaCO_3(s) \qquad K_{sp} = 5 \times 10^{-9}$$
$$Mg^{2+}(aq) + CO_3^{2-}(aq) \Leftrightarrow MgCO_3(s) \qquad K_{sp} = 2 \times 10^{-3}$$

Calcium carbonate, $CaCO_3(s)$, is often incorporated into the structures of the vast number of microorganisms that are the base of the oceanic food chain. Over millions of years, extensive deposits of limestone ($CaCO_3$) and dolomite (mixed $CaCO_3$ and $MgCO_3$) have been formed from these solids falling to the floor of prehistoric seas. Calcium carbonate is also the main constituent of marble, chalk, pearls, coral reefs, mollusk shells, and egg shells.
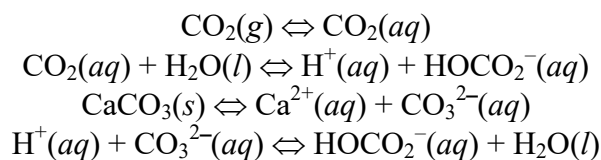
Although "insoluble" in water, calcium carbonate dissolves in acidic solutions. The carbonate ion behaves as a Brønsted base. The reaction with strong acids usually leads to the evolution of $CO_2(g)$ by this series of reactions.
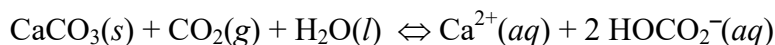
$$CaCO_3(s) \Leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$$
$$H^+(aq) + CO_3^{2-}(aq) \Leftrightarrow HOCO_2^-(aq) + H_2O(l)$$
$$H^+(aq) + HOCO_2^-(aq) \Leftrightarrow CO_2(aq) + H_2O(l)$$

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$$CO_2(aq) \Leftrightarrow CO_2(g)$$

All these equilibria are driven to the right by the presence of a high concentration of $H^+(aq)$ in the strong acid and loss of $CO_2(g)$ from the solution in the last step. These are the reactions that lead to the decay of statues and other structures made of marble or limestone exposed to "acid rain". Most acidic rain is formed by reaction of $SO_3(g)$, resulting from burning sulfur-containing coal in power plants, with water vapor to form dilute solutions of sulfuric acid, H_2SO_4 or $(HO)_2SO_2$, a strong acid.

We saw above that CO_2 dissolves in water to form a slightly acidic solution and this solution can also dissolve calcium carbonate.

$$CO_2(g) \Leftrightarrow CO_2(aq)$$
$$CO_2(aq) + H_2O(l) \Leftrightarrow H^+(aq) + HOCO_2^-(aq)$$
$$CaCO_3(s) \Leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$$
$$H^+(aq) + CO_3^{2-}(aq) \Leftrightarrow HOCO_2^-(aq) + H_2O(l)$$

The overall reaction is the sum of this series of reactions:

$$CaCO_3(s) + CO_2(g) + H_2O(l) \Leftrightarrow Ca^{2+}(aq) + 2\ HOCO_2^-(aq)$$

That is, the reactions produce a solution of calcium bicarbonate (or calcium hydrogen carbonate), a soluble salt.

This reaction often occurs underground when rainwater saturated with CO_2 seeps through a layer of limestone. As the water dissolves calcium carbonate, it forms openings in the limestone. Caves from which the limestone has been dissolved are often prevalent in areas where there are large deposits of $CaCO_3$ (for example, Mammoth Cave, Carlsbad Caverns, and Cave of the Mounds). If the water containing dissolved $Ca^{2+}(aq)$ and $HOCO_2^-(aq)$ reaches the ceiling of a cavern, the water will evaporate. As it evaporates, the concentrations of the ions increases and the reactions above begin to run in reverse — $CO_2(g)$ escapes and $CaCO_3(s)$ deposits on the ceiling. Over tens of thousands to millions of years, this deposit can grow into a stalactite (speleotherm), a limestone "icicle-like" structure hanging from the ceiling, Figure 4. If the solution drips to the floor of the cavern and evaporates there, it can build up into a stalagmite (sort of the mirror image of a stalactite). Given enough time, a stalactite and stalagmite below it can grow together to form a column.

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Figure 4. Stalactites, stalagmites, and columns formed by calcium carbonate deposition in Luray Caverns, a limestone cave in Virginia.

The amount of CO_2 that dissolves in seawater is controlled by the amount of $CO_2(g)$ in the atmosphere in contact with the surface. As the concentration of $CO_2(g)$ in the atmosphere has increased more has dissolved in the oceans, Figure 5A. About one-quarter of the CO_2 produced by human activities dissolves in the oceans. This drives the series of reactions above to the right, decreasing the amount of $CO_3^{2-}(aq)$, which puts a stress on the microorganisms that need $CaCO_3(s)$ to make their structures. Since these are vital as the base of the food chain for all the higher life in the ocean, upsetting them is a cause to worry about the increasing atmospheric CO_2. Along with the decrease in $CO_3^{2-}(aq)$ concentration, the concentration of base, $OH^-(aq)$, in the oceans is also decreasing. Although the oceans are still basic [more $OH^-(aq)$ than $H^+(aq)$], they have become less basic [decreased amount of $OH^-(aq)$ and increased $H^+(aq)$] and this is called "ocean acidification". This nomenclature can be confusing, so when you hear about "ocean acidification", remember this means seawater is becoming less basic, Figure 5B, and lower in carbonate concentration.
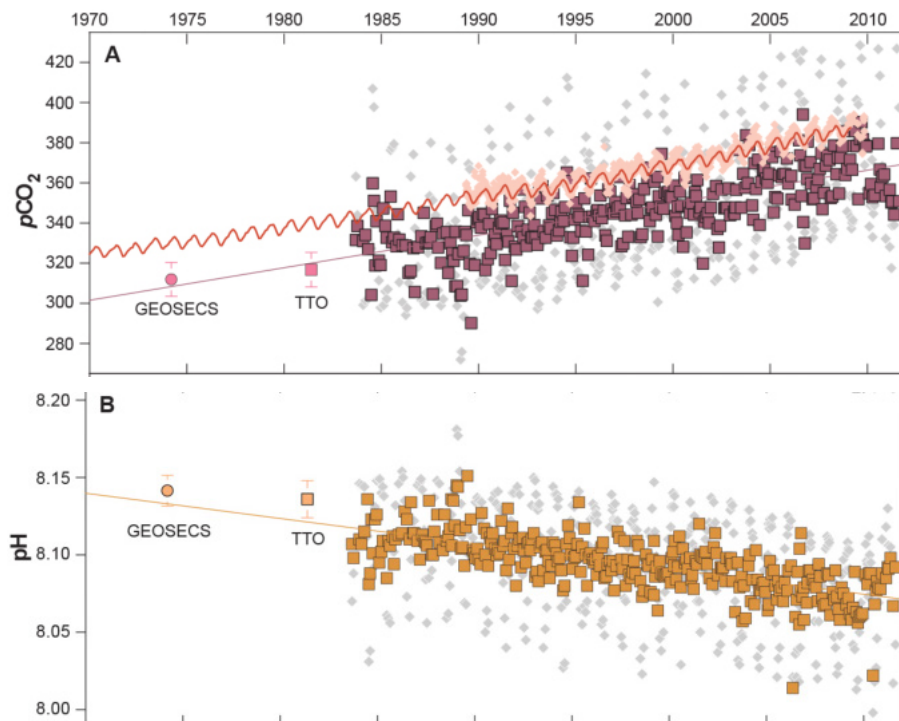
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Figure 5. (A) These data, from an oceanic experiment station near Bermuda, show increasing concentrations of CO_2 dissolved in seawater (dots) as the concentration in the atmosphere (the sawtooth Keeling curve) increases. (B) The pH decreases as the dissolved CO_2 increases. Decreasing pH means a decreasing amount of $OH^-(aq)$ relative to $H^+(aq)$.

Liquid Carbon Dioxide Dry Cleaning

Recently, some commercial dry cleaners have begun replacing the dry cleaning solvent perchloroethylene, $Cl_2C=CCl_2$, with liquid CO_2. Perchloroethylene is a possible carcinogen, and has been linked to bladder, esophogeal, and other cancers. CO_2 does not exist in liquid form at atmospheric pressure at any temperature. The pressure-temperature phase diagram of CO_2 shows that liquid carbon dioxide at 20°C requires a pressure of 30 atmospheres, Figure 6. The lowest pressure at which liquid CO_2 exists is at the triple point, 5.11 atm pressure at –56.6 °C.. The high pressures needed for liquid CO_2 require specialized washing machines. Clothing is immersed in liquid CO_2 in a highly pressurized cylinder and agitated by high-velocity fluid jets to remove soils, then dried in a high-velocity spin cycle. Liquid CO_2 has drawn high marks in *Consumer Reports'* tests for its cleaning results, and it is environmentally friendly (as long as it is recycled and not released to the atmosphere to add further to the greenhouse effect) since it produces no chlorinated pollutants.
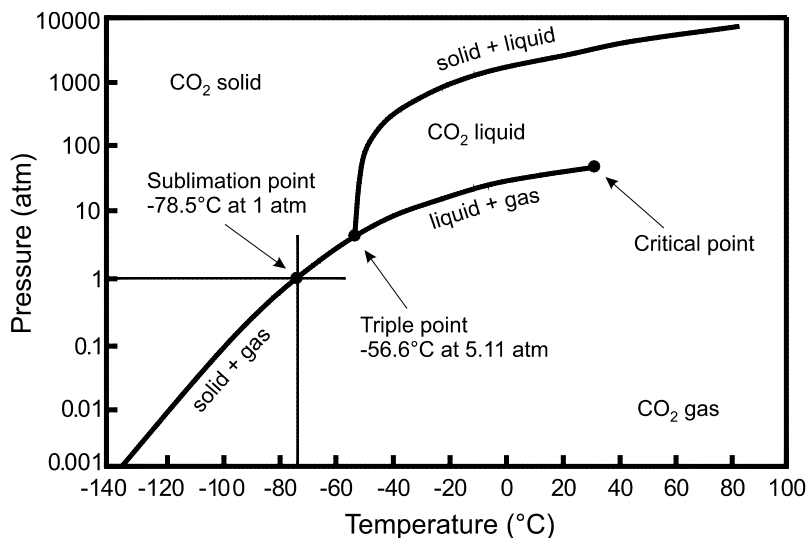
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Figure 6. The pressure-temperature phase diagram for CO_2 shows the conditions required to produce liquid CO_2 and hence the conditions required to use it as a dry cleaning solvent.

Photosynthesis, Respiration, and Carbon Dioxide

All the carbon atoms in the foods we eat and drink come originally from CO_2 in the atmosphere or dissolved in the Earth's waters. Converting CO_2 to food requires sunlight to provide the energy required for photosynthesis by green plants and photosynthetic microorganisms (especially in the oceans). The overall photosynthetic process produces carbohydrates (carbo = carbon + hydrate = water). In green plants the main product is glucose, $C_6H_{12}O_6$, which is used to make the plant's cellulose structure and used or stored as food (fuel for metabolic processes, both the plant's and for the animals, including us, that eat the plant). This overall photosynthetic process can be written as:

$$6\ CO_2 + 6\ H_2O + sunlight + catalysts \rightarrow C_6H_{12}O_6 + 6\ O_2$$
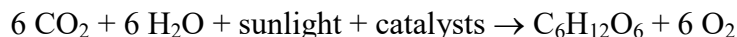
Not only is this process the origin of all our food, it also maintains the atmospheric oxygen we require to use the food to sustain our life. (Although it's not obvious from the reaction expression, the oxygen atoms in the molecular oxygen product come from the oxygen atoms in water.) The CO_2 reactant comes from the atmosphere and the H_2O from water vapor in the atmosphere or absorbed from the soil through the plant roots. As you might imagine, a large number of biological protein catalysts (enzymes) and partner molecules are required to guide the reactions that lead to this result. The most obvious of all these molecules is chlorophyll, which gives the plant (leaf) its green color and is responsible for the absorption of sunlight, which drives the overall reaction.

All the carbon atoms in the carbohydrates, fats, and proteins that maintain life on Earth are captured from CO_2 by photosynthesis. In the metabolic processes of life most of this carbon is eventually returned to the atmosphere as carbon dioxide. This can take a short time, as an insect, for example, eats some newly formed leaf and "burns" (metabolizes) its sugars for energy to keep moving. Or the cycle can take centuries as a tree grows, ages, dies, falls, and decays by the

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metabolic actions microorganisms that return carbon to the atmosphere. The biological cycle of CO_2 capture by photosynthesis and release via metabolism involves immense quantities of CO_2 flowing back and forth between the land and water and the atmosphere, as shown by the quantities in Figure 7.
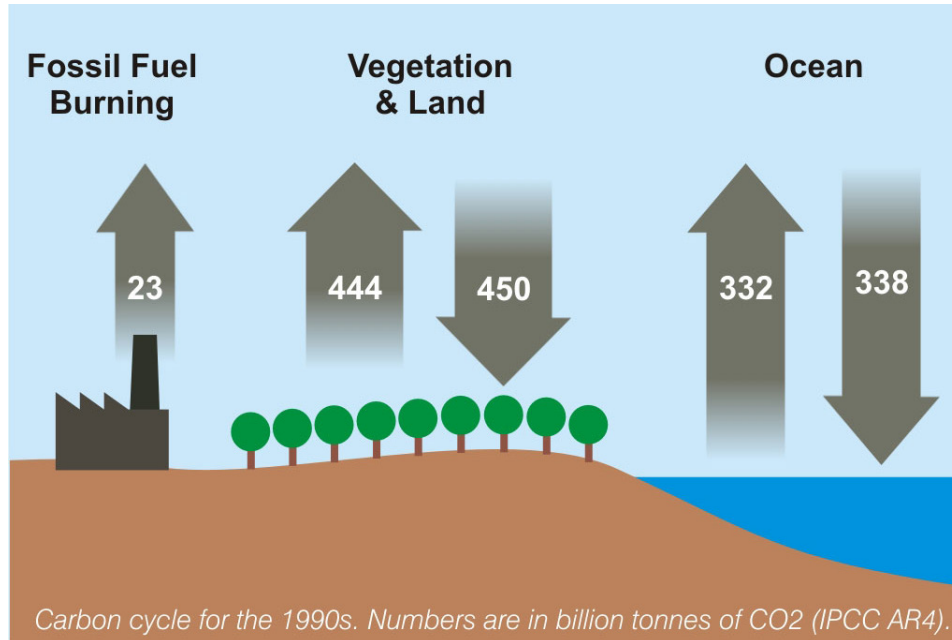

Carbon cycle for the 1990s. Numbers are in billion tonnes of CO2 (IPCC AR4).

Figure 7. This is a schematic representation of the flow of carbon (in billions of tonnes of CO_2) back and forth between sources on Earth's surface and the atmosphere each year. These data for the 1990s are based on data from the Fourth Report, 2007, of the Intergovernmental Panel on Climate Change. The numbers in the second decade of the 21st century are somewhat different (fossil fuel contribution increased by about 50%, for example), but the qualitative idea is the same—the sources produce more CO_2 than the sinks absorb each year (leading to the Keeling curve).

Source of the graphic is Skeptical Science website.

In addition to the natural exchange of CO_2 between the biosphere and the atmosphere, Figure 7 shows that human activity (mainly fossil fuel burning) is adding more CO_2 each year. Note that this is a one-way process not compensated by any human activity to remove any of the added CO_2. The carbon released by fossil fuel burning was captured by green plants millions of years ago and some of it ended up as coal, oil, and natural gas. Now we are adding it back to the environment and it ends up in the atmosphere, captured by photosynthesis, and dissolved in the oceans. Figure 7 shows that about a quarter of the fossil fuel CO_2 emitted each year ends up in land plants, about a quarter in the oceans (dissolved—ocean acidification—and taken up by photosynthetic phytoplankton), and about half remains and builds up in the atmosphere (giving the Keeling curve, global warming, and climate disruption).

The sawtooth character of the atmospheric CO_2 concentration in the Keeling curve shows that there is a yearly concentration oscillation. The representative annual variation shown in the inset from Figure 1 reproduced here:

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Annual Cycle
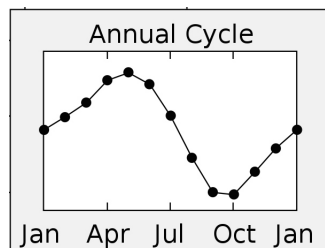
The actual values differ a bit from year to year, but the maximum to minimum difference in the concentration is about 6-7 ppm and seems to be independent of the overall increasing atmospheric CO_2 concentration. The maximum in the concentration usually occurs in late April and the minimum in October, six months later. Why?

There are large annual flows of CO_2 between the land biosphere and the atmosphere, Figure 7, but flow rates change with the seasons. The Keeling monitoring station is on Hawaii in the northern hemisphere, where most of Earth's land area is located. In spring and summer green plants, including agricultural crops, are growing and using CO_2 rapidly in photosynthesis. The metabolic decay processes can't keep up, so the net flow of CO_2 is from the atmosphere to the biosphere and atmospheric CO_2 falls. In fall and winter, green plants become dormant, farming stops, and the amount of photosynthesis drops. Now the decay processes become dominant and the net flow of CO_2 is from the biosphere to the atmosphere and atmospheric CO_2 rises.

Monitoring stations for CO_2 in the southern hemisphere show this same kind of seasonal variation, but not nearly as pronounced, because the majority of the hemisphere is ocean and the ocean biosphere does not vary so much with the seasons. The smaller variation is also masked a bit by mixing of the atmosphere between hemispheres. Mixing tends to even out variations in CO_2 concentrations, because the cycles are offset by six months (summer in the north is winter in the south).

All in all, carbon dioxide is an amazing compound. Who might have thought that such a simple molecule could have such a profound effect on an entire planet and that the planetary inhabitants could "accidentally" be using carbon dioxide to reshape the planet in uncontrollable ways.